



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/06866  <b>(22) International Filing Date:</b> 9 April 1998 (09.04.98)  <b>(30) Priority Data:</b> 08/833,878                      10 April 1997 (10.04.97)                      US  <b>(71) Applicant:</b> HENKEL CORPORATION [US/US]; Suite 200, Gulph Mills, PA 19406 (US).  <b>(72) Inventors:</b> HESSEL, J., Frederick; 2097 Country Club Drive, Doylestown, PA 18901 (US). SMITH, George, A.; 74 Mag- nolia Drive, Newtown, PA 18940 (US). ALLEN, Charles, B.; 167 Percy Court, East Norriton, PA 19403 (US). HANS- BERRY, Michael; 126 Shasta Road, Plymouth Meeting, PA 19462 (US). MAURER, Karl-Heinz; Dechenstrasse 5, D-40699 Erkrath (DE).  <b>(74) Agent:</b> TRZASKA, Steven, J.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CLEANING COMPOSITIONS HAVING ENHANCED ENZYME ACTIVITY  <b>(57) Abstract</b>  A cleaning composition containing: (a) from about 1 to about 60 % by weight of a surfactant component consisting essentially of: (i) a fatty alkyl ether sulfate; (ii) a linear alcohol ethoxylate; and (iii) a nonionic sugar surfactant, having a ratio by weight of (i):(ii):(iii) in a range of about 0.5 to 1.0:1.5 to 2.5:0.5 to 1.5; and (b) from about 0.1 to about 10 % by weight of an enzyme component selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof, all weights being based on the weight of the composition.		

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**CLEANING COMPOSITIONS HAVING ENHANCED ENZYME ACTIVITY****Field of the Invention:**

The present invention generally relates to a cleaning composition having enhanced enzyme activity and stability. More particularly, by adding an effective amount of an alkyl polyglycoside to a cleaning composition having a predetermined amount of enzyme contained therein, the enzyme activity and stability of the cleaning composition is enhanced.

**Background of the Invention:**

Enzymes have long been used in the detergent arts to enhance the cleaning of textile substrates. Specific stains on soiled fabrics are particularly responsive to enzymes which cleave specific linkages in the molecules of the stain. For example, enzymes such as proteases and lipases are effective for removing stains such as blood and oils from textile substrates. These stains are protein and lipid fractions from food and fats such as are

deposited from body soil. The action of the enzyme on the particular stain assists the surfactant to render overall cleaning improvement.

A particular difficulty associated with working with enzymes is that when they are presented in the form of powders, there have been instances of sensitization to the enzyme in selected individuals. To avoid contact with the enzymes, it has been proposed that the detergent products containing the same be prepared in the form of a liquid, thus minimizing the presence of any dust which may contain the enzyme. However, liquid detergent formulations containing enzymes cause problems relating to the stability of the enzyme. The problem associated with placing enzymes in a liquid environment is that they are subject to decomposition, either by surfactant denaturation or by self-digestion (proteolysis). It is therefore a problem to stabilize enzymes over extended periods of time, particularly when they are exposed to heat which further reduces enzyme stability.

It is therefore desirable to obtain a cleaning composition in a liquid or solid form in which the enzyme contained therein is stabilized such that enhanced synergistic cleaning performance is obtained.

#### Summary of the Invention:

The present invention provides a cleaning composition containing:

(a) from about 1 to about 60% by weight of a surfactant blend, the blend containing:

(i) an alkyl ether sulfate surfactant;  
(ii) a linear alcohol ethoxylate surfactant; and  
(iii) a nonionic sugar surfactant, wherein  
surfactants (i)-(iii) are present in the blend in a ratio  
5 by weight of (i):(ii):(iii) of about 1:2:1; and

(b) from about 0.1 to about 10% by weight of an enzyme  
selected from the group consisting of protease, amylase,  
lipase, cellulase, peroxidase, and mixtures thereof, all  
weights being based on the weight of the composition.

10 The present invention also provides a process for  
cleaning textile substrates involving contacting the  
textile substrates with the above-disclosed cleaning  
composition.

The present invention also provides a process for  
15 making a cleaning composition having enhanced enzyme  
stability involving:

(a) providing from about 1 to about 60% by weight of  
a surfactant blend, the blend containing:

(i) an alkyl ether sulfate surfactant;  
20 (ii) a linear alcohol ethoxylate surfactant; and  
(iii) a nonionic sugar surfactant, wherein  
surfactants (i)-(iii) are present in the blend in a ratio  
by weight of (i):(ii):(iii) of about 1:2:1;

(b) providing from about 0.1 to about 10% by weight of  
25 an enzyme selected from the group consisting of protease,  
amylase, lipase, cellulase, peroxidase, and mixtures  
thereof; and

(c) combining (a) and (b) to form the composition, all

weights being based on the weight of the composition.

Brief Description of the Drawings:

Fig. 1 is a phase diagram showing the stability of protease in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 2 is a phase diagram showing the stability of lipase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 3 is a phase diagram showing the stability of cellulase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 4 is a phase diagram showing the stability of a protease and lipase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 5 is a phase diagram showing the stability of a protease and cellulase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 6 is a phase diagram showing the stability of a lipase and cellulase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Fig. 7 is a phase diagram showing the stability of protease, lipase and cellulase in a cleaning composition in accordance with the present invention after 28 days at 40°C.

Description of the Invention:

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as being modified in all instances by the term "about".

Suitable nonionic sugar surfactants include, for example, alkyl polyglycosides and polyhydroxy fatty acid amides ("glucamides"). The polyhydroxy fatty acid amides which may be used in the present invention correspond to formula I:



wherein:  $\text{R}_1$  is H,  $\text{C}_1\text{-C}_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably  $\text{C}_1\text{-C}_4$  alkyl, more preferably  $\text{C}_1$  or  $\text{C}_2$  alkyl, most preferably  $\text{C}_1$  alkyl (i.e., methyl); and  $\text{R}_2$  is a  $\text{C}_5\text{-C}_{31}$  hydrocarbyl moiety, preferably straight chain  $\text{C}_7\text{-C}_{19}$  alkyl or alkenyl, more preferably straight chain  $\text{C}_9\text{-C}_{17}$  alkyl or alkenyl, most preferably straight chain  $\text{C}_{11}\text{-C}_{19}$  alkyl or alkenyl, or mixture thereof; and Y is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Y preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Y is a

glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Y. It should be understood that it is by no means intended to exclude other suitable raw materials. Y preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$ , where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ . Compounds of the formula I are also known as glucamides. Therefore, when, for example,  $R_1$  is methyl,  $R_2$  dodecyl; and Y is  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ , the compound in question is referred to as dodecyl N-methylglucamide.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, polyhydroxy fatty acid amides can be made by reductively aminating a reducing sugar reacting with an alkyl amine to form a corresponding N-alkyl polyhydroxyamine and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride to form the N-alkyl, polyhydroxy fatty acid amide.

The alkyl polyglycosides which can be used in the cleaning compositions according to the invention correspond



to formula II:



wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms;  $Z$  is a saccharide residue having 5 or 6 carbon atoms;  $b$  is a number having a value from 0 to about 12;  $a$  is a number having a value from 1 to about 6. Preferred alkyl polyglycosides which can be used in the compositions according to the invention have the formula I wherein  $Z$  is a glucose residue and  $b$  is zero. Such alkyl polyglycosides are commercially available, for example, as APG®, GLUCOPON®, or PLANTAREN® surfactants from Henkel Corporation, Ambler, PA 19002. Examples of such surfactants include but are not limited to:

1. GLUCOPON® 220 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and having an average degree of polymerization of 1.5.
2. GLUCOPON® 225 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and having an average degree of polymerization of 1.7.
3. GLUCOPON® 600 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.4.
4. GLUCOPON® 625 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.4.
5. APG® 325 Surfactant - an alkyl polyglycoside in which the alkyl group contains 9 to 11 carbon atoms and having an

average degree of polymerization of 1.6.

6. PLANTAREN® 2000 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 16 carbon atoms and having an average degree of polymerization of 1.4.

5 7. PLANTAREN® 1300 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.6.

8. AGRIMUL® PG 2067 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and  
10 having an average degree of polymerization of 1.7.

Other examples include alkyl polyglycoside surfactant compositions which are comprised of mixtures of compounds of formula I wherein Z represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; a is a  
15 number having a value from 1 to about 6; b is zero; and R<sub>1</sub> is an alkyl radical having from 8 to 20 carbon atoms. The compositions are characterized in that they have increased surfactant properties and an HLB in the range of about 10 to about 16 and a non-Flory distribution of glycosides,  
20 which is comprised of a mixture of an alkyl monoglycoside and a mixture of alkyl polyglycosides having varying degrees of polymerization of 2 and higher in progressively decreasing amounts, in which the amount by weight of polyglycoside having a degree of polymerization of 2, or  
25 mixtures thereof with the polyglycoside having a degree of polymerization of 3, predominate in relation to the amount of monoglycoside, said composition having an average degree of polymerization of about 1.8 to about 3. Such

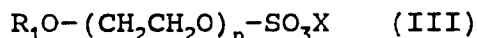
compositions, also known as peaked alkyl polyglycosides, can be prepared by separation of the monoglycoside from the original reaction mixture of alkyl monoglycoside and alkyl polyglycosides after removal of the alcohol. This separation may be carried out by molecular distillation and normally results in the removal of about 70-95% by weight of the alkyl monoglycosides. After removal of the alkyl monoglycosides, the relative distribution of the various components, mono- and poly-glycosides, in the resulting product changes and the concentration in the product of the polyglycosides relative to the monoglycoside increases as well as the concentration of individual polyglycosides to the total, i.e. DP2 and DP3 fractions in relation to the sum of all DP fractions. Such compositions are disclosed in U.S. patent 5,266,690, the entire contents of which are incorporated herein by reference.

Other alkyl polyglycosides which can be used in the compositions according to the invention are those in which the alkyl moiety contains from 6 to 18 carbon atoms in which the average carbon chain length of the composition is from about 9 to about 14 comprising a mixture of two or more of at least binary components of alkylpolyglycosides, wherein each binary component is present in the mixture in relation to its average carbon chain length in an amount effective to provide the surfactant composition with the average carbon chain length of about 9 to about 14 and wherein at least one, or both binary components, comprise a Flory distribution of polyglycosides derived from an

acid-catalyzed reaction of an alcohol containing 6-20 carbon atoms and a suitable saccharide from which excess alcohol has been separated.

In a particularly preferred embodiment, the nonionic  
5 sugar surfactant is an alkyl polyglycoside corresponding to formula II wherein  $R_1$  is a monovalent organic radical having from about 8 to about 16 carbon atoms,  $b$  is zero, and  $a$  is a number having a value of from 1 to about 3.

The alkyl ether sulfates which may be employed in the  
10 present invention correspond to formula III:



wherein  $R_1$  is a linear or branched alkyl or alkenyl radical having from about 8 to about 16 carbon atoms,  $n$  is a number from 1 to 10, and  $X$  is an alkali metal or alkaline earth  
15 metal. A particularly preferred alkyl ether sulfate for use in the present invention is SULFOTEX® NL60-S, a coconut mid-cut ether sulfate having 2 moles of ethylene oxide.

The linear alcohol ethoxylates which may be employed  
20 in the present invention can be either straight-chain or branched alcohols with 8 to 16 carbon atoms which are ethoxylated with from about 1 to about 10 moles of ethylene oxide. Their derivation is well known in the art.

In a particularly preferred embodiment of the present  
25 invention, the linear alcohol ethoxylate is a straight-chain  $C_{12}$ - $C_{16}$  alcohol ethoxylated with about 6 to about 7 moles of ethylene oxide.

The cleaning composition of the present invention also

contains from about 0.1 to about 10% by weight, and preferably about 0.5 to about 1.5% by weight of a deterative enzyme component. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, as well as mixtures thereof, all of which are employed on a pure enzyme basis. In a preferred embodiment, however, bacterial enzymes such as amylases and proteases, and fungal enzymes such as cellulases are employed in the cleaning composition. In a particularly preferred embodiment, the cleaning composition contains an enzyme component containing a mixture of a protease, cellulase and lipase.

Examples of suitable lipases for use herein include those of animal, plant, and microbiological origin. Although only limited studies on lipase distribution in plants have been conducted, suitable lipase enzymes are present in cambium, bark, and in plant roots. In addition, lipases have been found in the seeds of fruit, oil palm, lettuce, rice, bran, barley and malt, wheat, oats and oat flour, cotton tung kernels, corn, millet, coconuts, walnuts, fusarium, cannabis and cucurbit.

Suitable lipases are also found in many strains of bacteria and fungi. For example, lipases suitable for use herein can be derived from Pseudomonas, Aspergillus, Pneumococcus, Staphylococcus, and Staphylococcus Toxins, Mycobacterium Tuberculosis, Mycotorula Lipolytica and Sclerotinia microorganisms.

Suitable animal lipases are found in the body fluids

and organs of many species. Most organs of mammals contain lipases, but in addition, the enzymes are found in several digestive juices as well as in pancreatic juice.

5 Amylases suitable for use in the present cleaning composition include, for example,  $\alpha$ -amylases obtained from a special strain of *B.licheniformis*. Amylolytic proteins include, for example, RAPIDASE®, available from International Bio-Synthetics, Inc. and TERMAMYL®, available from Novo Industries.

10 Cellulases which may be employed herein include both bacterial and fungal cellulases. Examples include cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800, and cellulases produced by a  
15 fungus of *Bacillus N* or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula Solander*).

Peroxidase enzymes are used in combination with oxygen  
20 sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching", i.e. to prevent the transfer of dyes or pigments removed from textile substrates during washing operations to other substrates in the wash solution.  
25 Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase.

Suitable proteolytic enzymes for use in the cleaning

composition of the present invention are of vegetable, animal, bacterial, mold and fungal origin. Examples of proteases which may be employed in the cleaning composition of the present invention are the subtilisins which are  
5 obtained from particular strains of *B.subtilis* and *B.licheniforms*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®.

10 Of particular interest in the category of proteolytic enzymes are the alkaline proteases derived from *Bacillus lentus* hereinafter referred to as BLAP, as disclosed in U.S. Pat. No. 5,352,604, the entire contents of which is hereby incorporated by reference.

15 The surfactant blend, as previously discussed, is employed in the present composition in an amount of from about 1 to about 60% by weight, and preferably from about 5 to about 50% by weight, and most preferably from about 15 to about 30% by weight, based on the weight of the cleaning  
20 composition. The ratio by weight of fatty alkyl ether sulfate:linear alcohol ethoxylate:nonionic sugar surfactant is in the range of from about 0.5 to 1.0:1.5 to 2.5:0.5 to 1.5. In a particularly preferred embodiment, the ratio by weight is about 1:2:1.

25 The enzyme component employed herein is present in the cleaning composition in an amount of from about 0.1 to about 10%, and preferably from about 0.5 to about 1.5% by weight, based on the weight of the composition. The enzyme

component preferably consists of a mixture of protease, lipase and cellulase.

According to one embodiment of the invention, there is provided a cleaning composition containing: (a) from about  
5 15 to about 30% by weight of a surfactant component consisting essentially of: (i) a fatty alkyl ether sulfate, (ii) a linear alcohol ethoxylate, and (iii) an alkyl polyglycoside, in a ratio by weight of (i):(ii):(iii) of about 1:2:1; and (b) from about 0.5 to about 1.5% by  
10 weight, of an enzyme component consisting essentially of mixture of a protease, a lipase and a cellulase.

The cleaning composition of the present invention may also contain auxiliary components selected from the group consisting of other anionic surfactants, other nonionic  
15 detergent surfactants, cationic surfactants, amphoteric and zwitterionic surfactants, detergent builders, bleaching agents, bleaching activators, polymeric soil release agents, chelating agents, anti-redeposition agents, polymeric dispersing agents, optical brighteners, foam  
20 inhibitors, carriers, hydrotropes, processing aids, dyes, pigments, solvents for liquid formulations, and mixtures thereof.

The present invention also provides a process for cleaning textile substrates involving contacting the  
25 textile substrates with above-disclosed cleaning composition.

The present invention also provides a process for making a cleaning composition having enhanced cleaning



properties involving: (a) providing from about 1 to about 60% by weight, preferably from about 5 to about 50% by weight, and most preferably from about 15 to about 30% by weight, of a surfactant blend, the blend containing: (i) an alkyl ether sulfate surfactant; (ii) a linear alcohol ethoxylate surfactant; and (iii) a nonionic sugar surfactant, wherein the ratio by weight of (i):(ii):(iii) is about 1:2:1; (b) providing from about 0.5 to about 1.5% by weight of an enzyme component consisting essentially of a mixture of a protease, a lipase, and a cellulase; and (c) combining (a) and (b) to form the composition, all weights being based on the weight of the composition.

The present invention will be better understood from the examples which follow, all of which are intended to be illustrative only and not meant to unduly limit the scope of the invention. Unless otherwise indicated, percentages are on a weight-by-weight basis.

#### EXAMPLES

To test the effect of different surfactants on long term enzyme stability in a formulated liquid detergent, an experimental design approach was used. Detergent samples were prepared using a combination of different surfactants holding the surfactant activities constant at 26%. In this work, three different types of enzymes were used. The activity of each enzyme in the formulation was determined at time zero and as a function of time at elevated temperature (40°C). The stability of each enzyme is

expressed in percentage units based on the initial enzyme activity.

The formulation and the range for each component is given in Table 1 below. EMERY® 625 is a coconut fatty acid  
5 used for foam control. Monoethanolamine is used to neutralize the fatty acid and as an alkalinity source. Propylene glycol/sodium borate is added to help stabilize the enzymes. The enzymes are added to the propylene glycol/sodium borate mixture prior to addition to the  
10 detergent base. The pH of the formulated detergent is adjusted to 8.5 prior to adding the enzymes.

Table 1. Liquid Detergent Formulation for Experimental Design Experiments.

	Ingredients	Weight Percent
	SULFOTEX® NL60-S	0 - 19%
5	BIOSOFT® D-40	0 - 19%
	NEODOL® 25-7	0 - 13%
	GLUCOPON® 600UP	0 - 13%
	EMERY® 625	4.0%
	Monoethanolamine	1.0%
10	Sodium Sulfate	0.1%
	Ethanol	4.5%
	Propylene Glycol/ Sodium Borate (7/1)	15%
	SAVINASE® 16L	0.75%
15	LIPOLASE® 100L	0.75%
	CAREZYME®	0.75%

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	SULFOTEX® NL60-S = 60% FAES supplied by Henkel Corp.
	BIOSOFT® D-40 = 40% LAS supplied by Stepan
20	NEODOL® 25-7 = 100% LAE supplied by Shell Chemical
	GLUCOPON® 600UP = 50% APG supplied by Henkel Corp.
	EMERY® 625 = a coconut fatty acid supplied by Henkel Corp.
	SAVINASE® 16L = solution grade protease supplied by Novo Nordisk
25	LIPOLASE® 100L = solution grade lipase supplied by Novo Nordisk
	CAREZYME® = solution grade cellulase supplied by Novo Nordisk

30 The stability of protease after 28 days at 40°C is shown in Figure 1. The stability of the enzyme is given

along the z axis while the xy base plane gives the surfactant composition. For protease, enzyme activity increases with increasing concentration of FAES and decreases with increasing concentration of LAS. Increasing  
5 the concentration of GLUCOPON® 600UP in the blend gives a slight improvement in enzyme stability.

The stability of lipase after 28 days at 40°C is shown in Figure 2. For this system, enzyme stability increases with increasing concentration of LAE and APG and decreases  
10 with increasing concentration of FAES and LAS. It appears that anionic surfactants are effective at denaturing the protein.

The stability of cellulase at 28 days at 40°C is shown in Figure 3. For this system, enzyme stability increases with increasing concentration of FAES, LAE and APG and  
15 decreases with increasing concentration of LAS in the formulation.

To determine the optimum surfactant composition for multiple enzyme systems, the data from the design  
20 experiments was solved simultaneously. The optimum surfactant composition for protease and lipase is shown in Figure 4. The unshaded area represents the surfactant blend ratio giving good stability for both enzymes. Based on this work, the optimum blend consists of FAES/LAE/APG =  
25 25%/50%/25%.

The optimum surfactant composition for protease and cellulase is given in Figure 5. Again the unshaded region represents regions with good stability for both enzymes.

Based on this work, the optimum surfactant blend ratio consists of FAES/LAE/APG/LAS = 30%/50%/10%/10%.

The optimum surfactant composition for lipase and cellulase is given in Figure 6. The optimum surfactant  
5 blend ratio consists of FAES/LAE/APG/LAS = 10%/50%/35%/5%.

The optimum surfactant composition for protease, lipase and cellulase is given in Figure 7. The optimum blend ratio consists of FAES/LAE/APG = 25%/50%/25%.

**What is claimed is:**

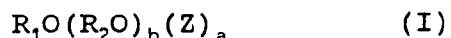
## 1. A cleaning composition comprising:

(a) from about 1 to about 60% by weight of a surfactant component consisting essentially of:

- 5 (i) a fatty alkyl ether sulfate;  
(ii) a linear alcohol ethoxylate; and  
(iii) a nonionic sugar surfactant, having a ratio by weight of (i):(ii):(iii) in a range of about 0.5 to 1.0:1.5 to 2.5:0.5 to 1.5; and

10 (b) from about 0.1 to about 10% by weight of an enzyme component selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof, all weights being based on the weight of the composition.

15 2. The composition of claim 1 wherein the nonionic sugar surfactant is selected from the group consisting of an alkyl polyglycoside corresponding to formula I:



wherein  $R_1$  is a monovalent organic radical having from about  
20 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6, a polyhydroxy fatty acid amide, and mixtures  
25 thereof.

3. The composition of claim 2 wherein the nonionic sugar surfactant is an alkyl polyglycoside of formula I wherein  $R_1$  is a monovalent organic radical having from about 8 to

about 16 carbon atoms, b is zero, and a is a number having a value of from 1 to about 3.

4. The composition of claim 1 wherein the surfactant component is present in the composition in an amount of  
5 from about 15 to about 30% by weight, based on the weight of the composition.

5. The composition of claim 1 wherein the ratio by weight of (i):(ii):(iii) is about 1:2:1.

6. The composition of claim 1 wherein the enzyme  
10 component consists essentially of a protease, a lipase and a cellulase.

7. The composition of claim 1 wherein the enzyme component is present in the composition in an amount of from about 0.5 to about 1.5% by weight, based on the weight  
15 of the composition.

8. The composition of claim 1 wherein the composition further comprises an auxiliary component selected from the group consisting of other anionic surfactants, other nonionic surfactants, cationic surfactants, amphoteric and  
20 zwitterionic surfactants, detergent builders, bleaching agents, bleaching activators, polymeric soil release agents, chelating agents, anti-redeposition agents, polymeric dispersing agents, optical brighteners, foam inhibitors, carriers, hydrotropes, processing aids, dyes,  
25 pigments, solvents for liquid formulations, and mixtures thereof.

9. The composition of claim 1 wherein (i) is present in the surfactant blend in an amount of about 25% by weight,

(ii) is present in the surfactant blend in an amount of about 50% by weight, and (iii) is present in the surfactant blend in an amount of about 25% by weight, all weights being based on the total weight of the surfactant blend.

5 10. The composition of claim 1 wherein the protease is BLAP.

11. The composition of claim 1 wherein the fatty alkyl ether sulfate is coconut mid-cut ether sulfate having about 2 moles of ethylene oxide.

10 12. The composition of claim 1 wherein the linear alcohol ethoxylate is coconut mid-cut ether sulfate having about 7 moles of ethylene oxide.

13. A process for cleaning a textile substrate comprising contacting the textile substrate with a cleaning  
15 composition comprising:

(a) from about 1 to about 60% by weight of a surfactant component consisting essentially of:

(i) a fatty alkyl ether sulfate;

(ii) a linear alcohol ethoxylate; and

20 (iii) a nonionic sugar surfactant, having a ratio by weight of (i):(ii):(iii) in a range of about 0.5 to 1.0:1.5 to 2.5:0.5 to 1.5; and

(b) from about 0.1 to about 10% by weight of an enzyme component selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases, and mixtures  
25 thereof, all weights being based on the weight of the composition.

14. The process of claim 13 wherein the nonionic sugar



surfactant is selected from the group consisting of an alkyl polyglycoside corresponding to formula I:



wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms;  $Z$  is a saccharide residue having 5 or 6 carbon atoms;  $b$  is a number having a value from 0 to about 12;  $a$  is a number having a value from 1 to about 6, a polyhydroxy fatty acid amide, and mixtures thereof.

15. The process of claim 14 wherein the nonionic sugar surfactant is an alkyl polyglycoside of formula I wherein  $R_1$  is a monovalent organic radical having from about 8 to about 16 carbon atoms,  $b$  is zero, and  $a$  is a number having a value of from 1 to about 3.

16. The process of claim 13 wherein the surfactant component is present in the composition in an amount of from about 15 to about 30% by weight, based on the weight of the composition.

17. The process of claim 13 wherein the ratio by weight of (i):(ii):(iii) is about 1:2:1.

18. The process of claim 13 wherein the enzyme component consists essentially of a protease, a lipase and a cellulase.

19. The process of claim 13 wherein the enzyme component is present in the composition in an amount of from about 0.5 to about 1.5% by weight, based on the weight of the composition.

20. The process of claim 13 wherein the composition further comprises an auxiliary component selected from the group consisting of other anionic surfactants, other nonionic surfactants, cationic surfactants, amphoteric and zwitterionic surfactants, detergent builders, bleaching agents, bleaching activators, polymeric soil release agents, chelating agents, anti-redeposition agents, polymeric dispersing agents, optical brighteners, foam inhibitors, carriers, hydrotropes, processing aids, dyes, pigments, solvents for liquid formulations, and mixtures thereof.

21. The process of claim 13 wherein (i) is present in the surfactant blend in an amount of about 25% by weight, (ii) is present in the surfactant blend in an amount of about 50% by weight, and (iii) is present in the surfactant blend in an amount of about 25% by weight, all weights being based on the total weight of the surfactant blend.

22. The process of claim 13 wherein the protease is BLAP.

23. The process of claim 13 wherein the fatty alkyl ether sulfate is coconut mid-cut ether sulfate having about 2 moles of ethylene oxide.

24. The process of claim 13 wherein the linear alcohol ethoxylate is a coconut mid-cut ether sulfate having about 7 moles of ethylene oxide.

25. A process for making a cleaning composition having enhanced enzyme stability comprising:

(a) providing from about 1 to about 60% by weight of a surfactant component consisting essentially of:

(i) a fatty alkyl ether sulfate;  
(ii) a linear alcohol ethoxylate; and  
(iii) a nonionic sugar surfactant, having a ratio  
by weight of (i):(ii):(iii) in a range of about 0.5 to  
5 1.0:1.5 to 2.5:0.5 to 1.5;

(b) providing from about 0.1 to about 10% by weight of  
an enzyme component selected from the group consisting of  
proteases, amylases, lipases, cellulases, peroxidases, and  
mixtures thereof, all weights being based on the weight of  
10 the composition; and

(c) mixing (a) and (b) to form the composition.

26. The process of claim 25 wherein the nonionic sugar  
surfactant is selected from the group consisting of an  
alkyl polyglycoside corresponding to formula I:



wherein  $R_1$  is a monovalent organic radical having from about  
6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene  
radical having from 2 to 4 carbon atoms; Z is a saccharide  
residue having 5 or 6 carbon atoms; b is a number having a  
20 value from 0 to about 12; a is a number having a value from  
1 to about 6, a polyhydroxy fatty acid amide, and mixtures  
thereof.

27. The process of claim 26 wherein the nonionic sugar  
surfactant is an alkyl polyglycoside of formula I wherein  
25  $R_1$  is a monovalent organic radical having from about 8 to  
about 16 carbon atoms, b is zero, and a is a number having  
a value of from 1 to about 3.

28. The process of claim 25 wherein the surfactant

component is present in the composition in an amount of from about 15 to about 30% by weight, based on the weight of the composition.

29. The process of claim 25 wherein the ratio by weight of  
5 (i):(ii):(iii) is about 1:2:1.

30. The process of claim 25 wherein the enzyme component consists essentially of a protease, a lipase and a cellulase.

31. The process of claim 25 wherein the enzyme component  
10 is present in the composition in an amount of from about 0.5 to about 1.5% by weight, based on the weight of the composition.

32. The process of claim 25 wherein the composition further comprises an auxiliary component selected from the  
15 group consisting of other anionic surfactants, other nonionic surfactants, cationic surfactants, amphoteric and zwitterionic surfactants, detergent builders, bleaching agents, bleaching activators, polymeric soil release agents, chelating agents, anti-redeposition agents,  
20 polymeric dispersing agents, optical brighteners, foam inhibitors, carriers, hydrotropes, processing aids, dyes, pigments, solvents for liquid formulations, and mixtures thereof.

33. The process of claim 25 wherein (i) is present in the  
25 surfactant blend in an amount of about 25% by weight, (ii) is present in the surfactant blend in an amount of about 50% by weight, and (iii) is present in the surfactant blend in an amount of about 25% by weight, all weights being

based on the total weight of the surfactant blend.

34. The process of claim 25 wherein the protease is BLAP.

35. The process of claim 25 wherein the fatty alkyl ether  
sulfate is a coconut mid-cut ether sulfate having about 2  
5 moles of ethylene oxide.

36. The process of claim 25 wherein the linear alcohol  
ethoxylate is a coconut mid-cut ether sulfate having about  
7 moles of ethylene oxide.

37. The product of the process of claim 25.

10 38. The product of the process of claim 26.

39. The product of the process of claim 27.

40. The product of the process of claim 28.

41. The product of the process of claim 29.

42. The product of the process of claim 30.

15 43. The product of the process of claim 31.

44. The product of the process of claim 32.

45. The product of the process of claim 33.

46. The product of the process of claim 34.

47. The product of the process of claim 35.

20 48. The product of the process of claim 36.

DESIGN-EXPERT PLOT

MODEL:  
QUADRATIC

ACTUAL COMPONENTS

X1 = FAES

X2 = LAS

X3 = 600

ACTUAL CONSTANTS:

LAE = 13.00

RESPONSE: SAVINASE 28

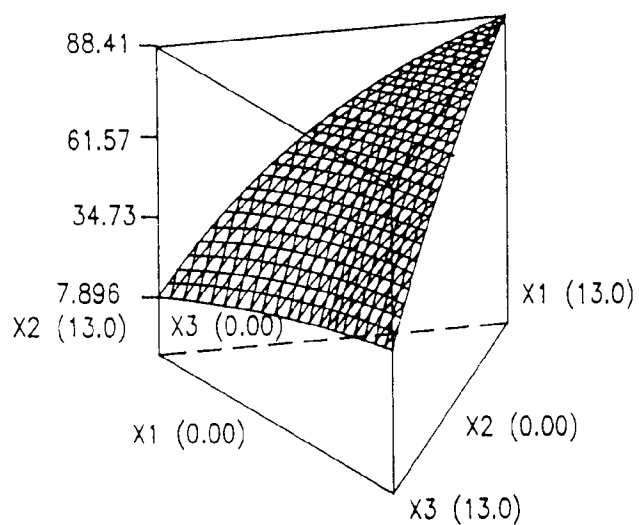


FIG. 1

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DESIGN-EXPERT PLOT

MODEL:  
QUADRATIC

ACTUAL COMPONENTS:

X1 = FAES

X2 = LAS

X3 = 600

ACTUAL CONSTANTS:

LAE = 13.00

RESPONSE: LIPASE 28

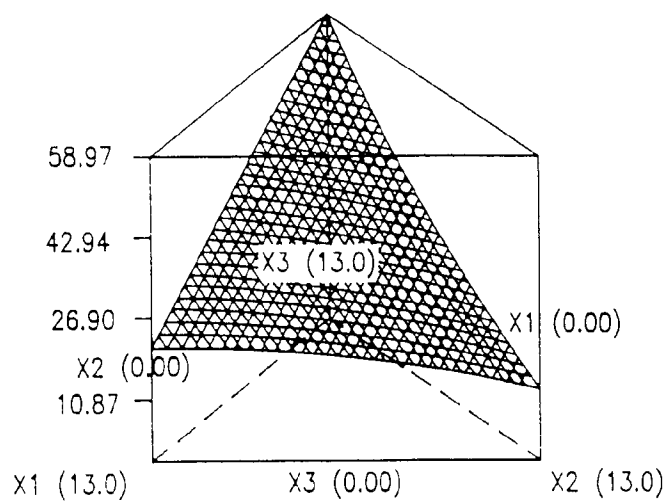


FIG. 2

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DESIGN-EXPERT PLOT  
MODEL:  
QUADRATIC

RESPONSE: CELLULASE28

ACTUAL COMPONENTS:  
X1 = FAES  
X2 = LAS  
X3 = 600  
ACTUAL CONSTANTS:  
LAE = 13.00

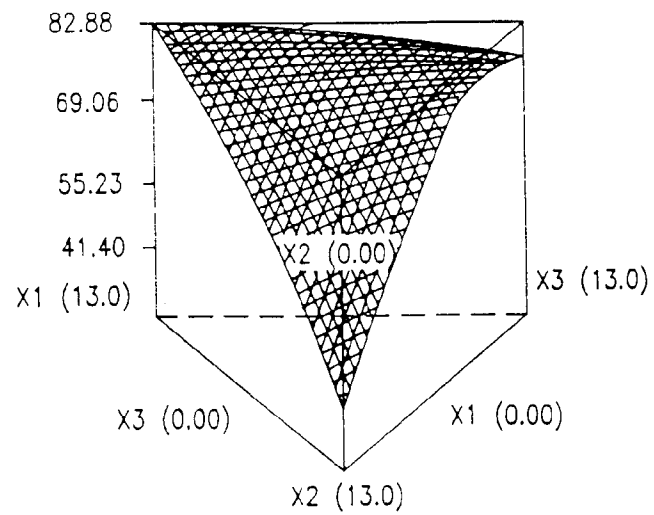


FIG. 3



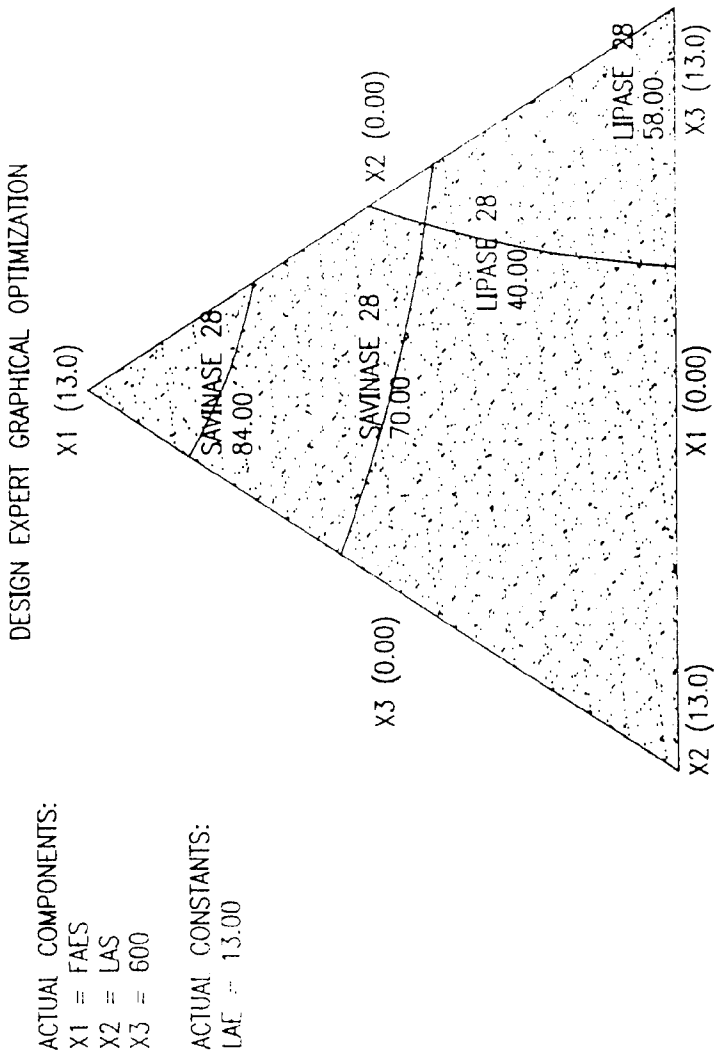


FIG. 4

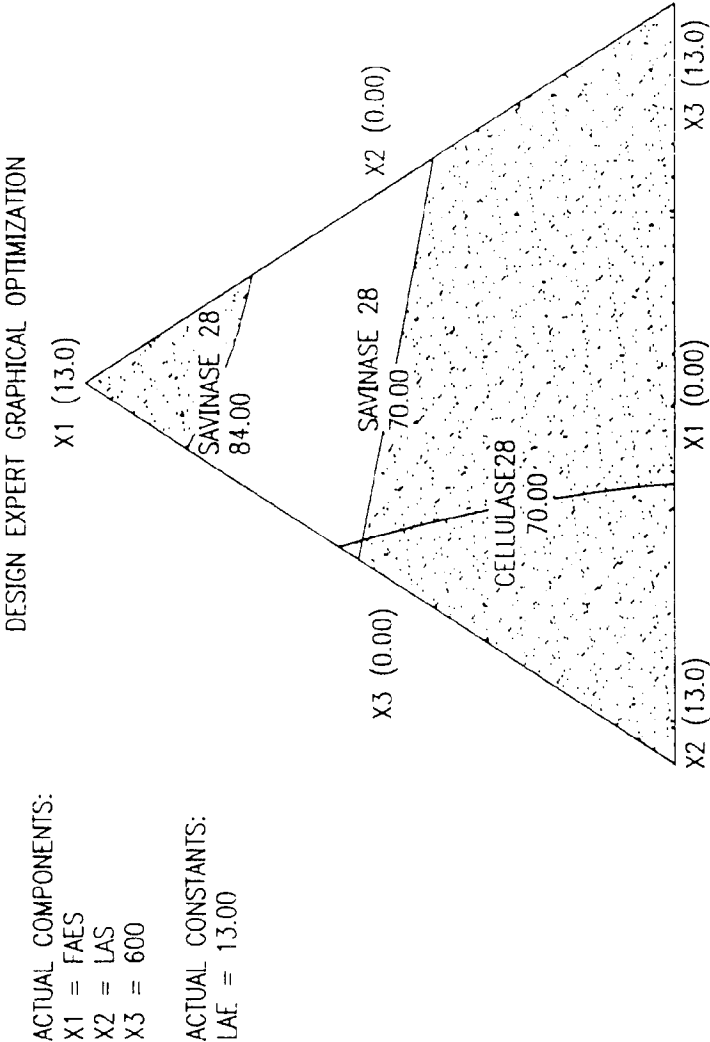


FIG. 5

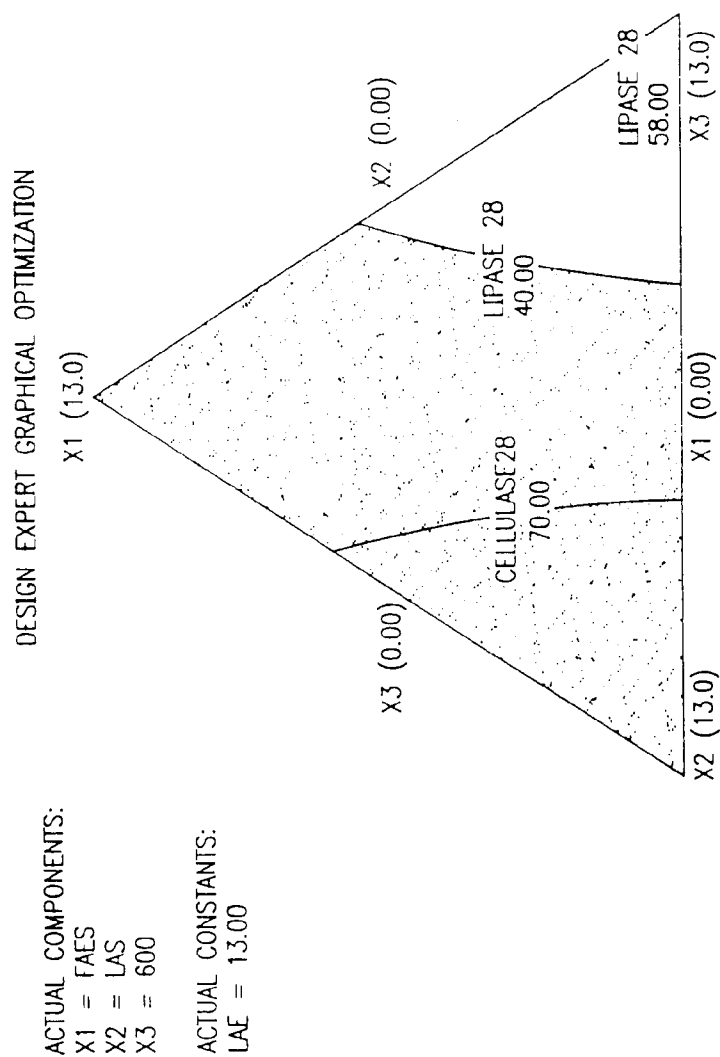


FIG. 6

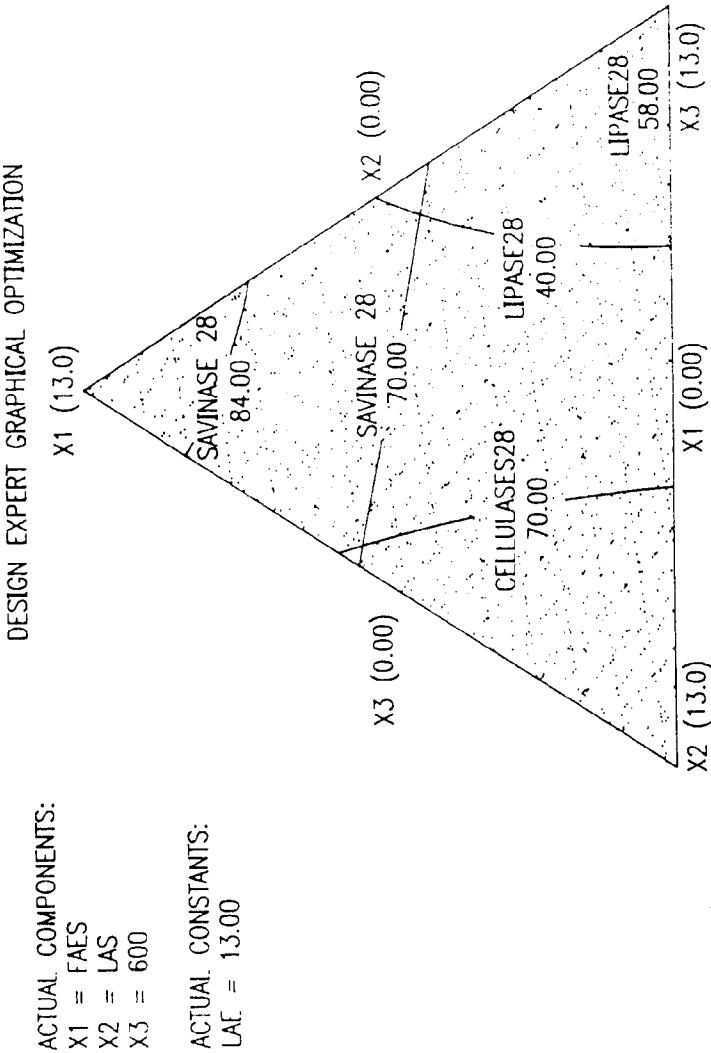


FIG. 7

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/06866

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/386

US CL :510/ 299, 320, 321, 392, 393, 424

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/ 299, 320, 321, 392, 393, 424

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: SULFATE#, NONIONIC, LIPASE#, CELLULASE#

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,707,950 A (KASTURI ET AL) 13 January 1998, columns 2-columns 4, claims and examples	1-48
Y,P	US 5,703, 032 A (MYONGSUK BAE-LEE ET AL) 30 December 1997, abstract; columns 1-4 and examples.	1-48
Y,P	US 5,677, 272 A (GHOSH ET AL) 14 October 1997, abstract columns 2-6 and claims.	1-48
Y	US 5,587,356 A (DAUDERMAN ET AL) 24 December 1996, columns 2 lines 2-30, columns 3 lines 1-49; claims and examples.	1-48
Y	US H 1,468 A (COSTA ET AL) 01 August 1995, columns 1-column 5, examples and claims.	1-48



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 MAY 1998

Date of mailing of the international search report

21 JUL 1998

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US98/06866

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,332,528 A (PAN ET AL) 26 JULY 1994, see entire document.	1-48